DoD Laboratory Assessments: Top Ten Findings

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Background

- **HQUSACE Policy Memo dated 30-Sep-2004**

  Directed USACE components to implement DoD *Quality Systems Manual for Environmental Laboratories (QSM)* by specification in contracts for HTRW projects.

- **USACE EMCX has assessed ≈ 40 labs for compliance with QSM V3 since 2006**

- **Common findings were based on:**

  - **Project requirements**
  - **Analytical methods**
  - **Good lab practice**
  - **DoD QSM V3**
  - **Scientific principles**

10 – Method Blank

- **Problem**: Acceptance criteria “MB < RL”
- **Impact**: Bias
- **Rationale**: Data uncertainty not considered
- **Solution**: MB < ½ RL; MB < RL for common contaminants
- **Reference**: QSM Box D-5 (*Box D-1*)*

*** QSM V3 in regular font and QSM V4 in *italic font***

10 – Method Blank (cont)

- **QSM V3, Box D-5**

  "If the method blank contamination exceeds <u>one-half the reporting limit</u>, the laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria. The concentrations of common laboratory contaminants shall not exceed the <u>reporting limit</u>."

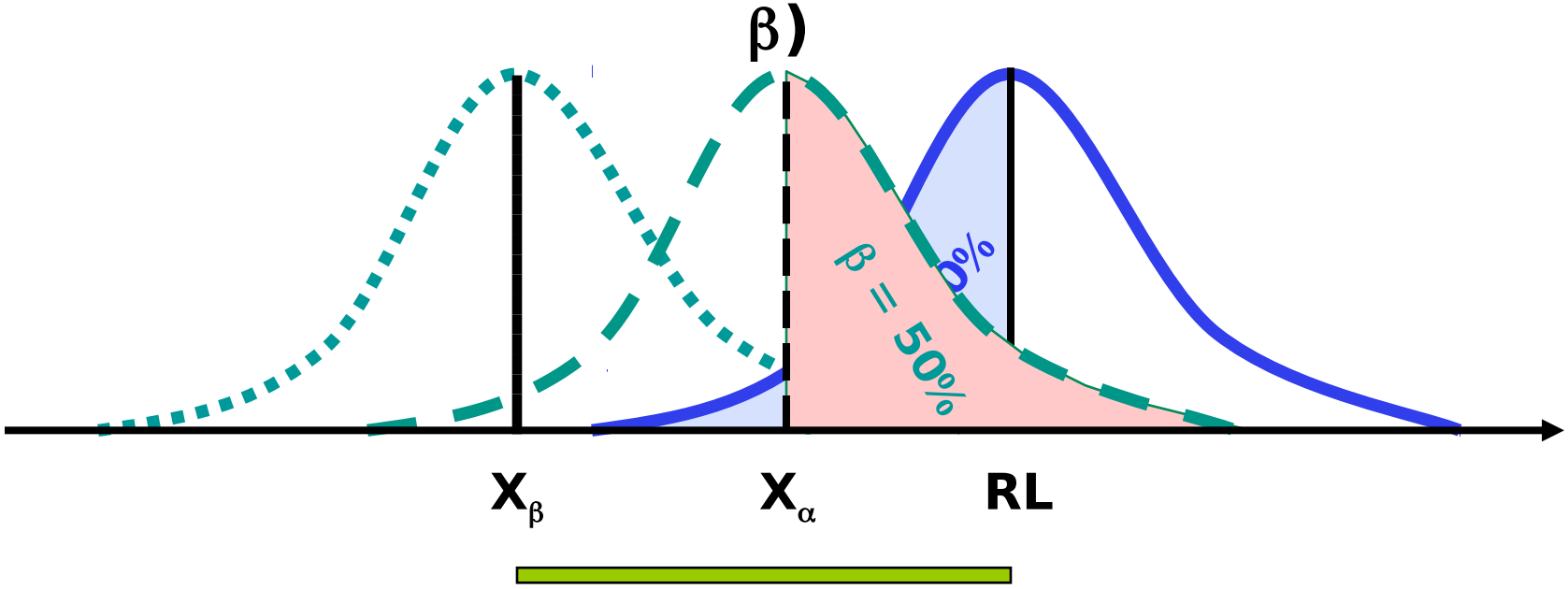
- ***QSM V4, Box D-1***

  "The concentration of any target analytes in the blank exceeds <u>1/2 the reporting limit</u> AND is greater than 1/10 the amount measured in any samples or 1/10 of the regulatory level (whichever is greater); the concentration of any common laboratory contaminants in the blank exceeds the <u>reporting limit</u> AND…"

10 – Method Blank (cont)

Data Uncertainty and Decision Errors

H_0: $X \geq RL$, H_A: $X < RL$, Decision Errors (α, β)

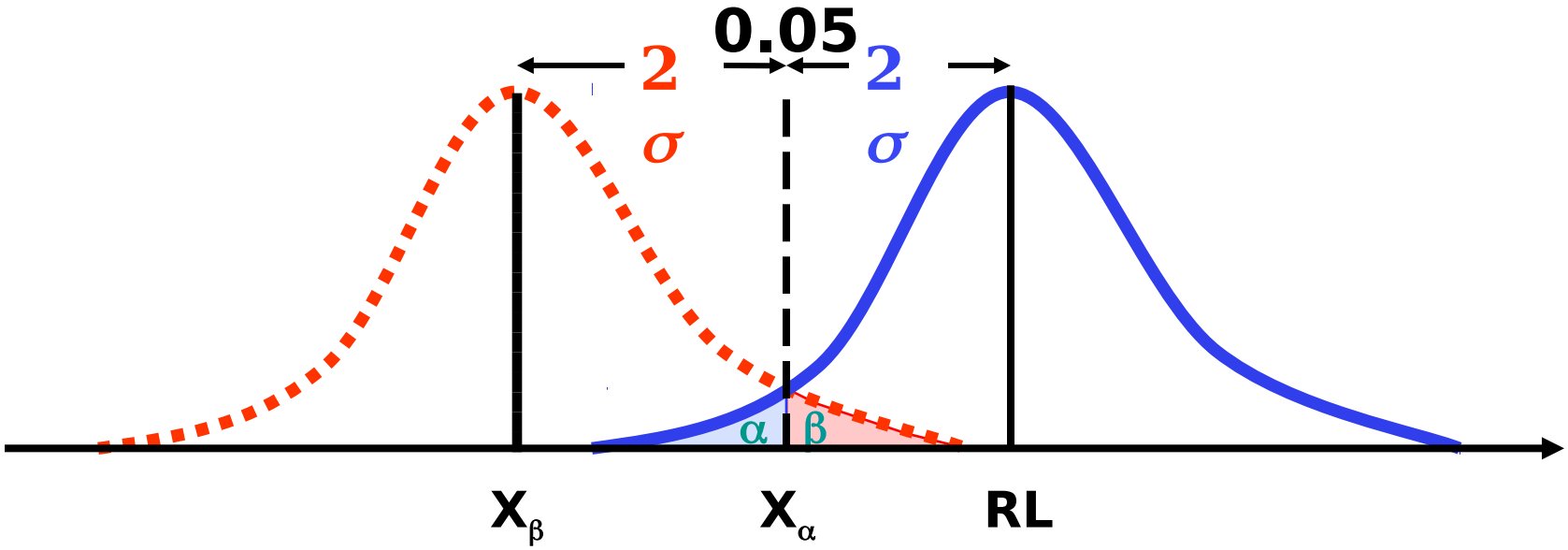


$\Delta = RL - X_\beta = f$(Data Quality, Decision Errors)

10 – Method Blank (cont)

Data Uncertainty and Decision Errors

If CL_{LCS} = 70 – 130% & Decision Errors $\alpha = \beta =$ 0.05



$$X_\beta = RL - \Delta = RL - 4\sigma \approx RL - 50\% \times RL = \tfrac{1}{2}\, RL$$

9 – ICSA

- **Problem**: Acceptance criteria "< ± 20%"
- **Impact**: Bias
- **Rationale**: Potentially wrong interelement interference correction factor
- **Solution**: Absolute value of all non-spiked analytes < 2 × MDL, unless verified impurity
- **Reference**: QSM Tables B-6/B-7 (*Tables F-7/ F-8*) & Method 6010C, Sec 4.2.9

9 – ICSA (cont)

- **QSM V3, Tables B-6/B-7**

  "ICS-A: Absolute value of concentration for all non-spiked analytes < 2 x MDL (unless they are a verified trace impurity from one of the spiked analytes)."

- ***QSM V4, Tables F-7/F-8***

  "ICS-A: Absolute value of concentration for all non-spiked analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes)."

9 – ICSA (cont)

- **Method 6010C, Section 4.2.9**

  "Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference."

- **Method 6010C, Section 4.2.10.1**

  "One method to verify the absence of interferences is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval)."

8 – Spike Standards

- **Problem**: Prepare spike standards in a non-water-miscible solvent
- **Impact**: Bias
- **Rationale**: High biased spike recovery
- **Solution**: Prepare spike standards in a water-miscible solvent
- **Reference**: Method 3500C, Sec 7.4

8 – Spike Standards (cont)

- **Method 3500C, Section 7.4**

7.4 Stock standards for spiking solutions -- The stock solutions used for the calibration standards are acceptable (dilutions must be made in a water-miscible solvent) except for the quality control check sample stock concentrate which must be prepared independently to serve as a check on the accuracy of the calibration solution.

7.4.1 Dissolve the compound in a water-miscible solvent (i.e., methanol, acetone, 2-propanol, etc.) and dilute to volume in a 10-mL volumetric flask.

7 – Spike Additions

- **Problem**: Add spikes after sample processing
- **Impact**: Precision & bias
- **Rationale**: Spiked compounds should mimic the compounds already present in field samples
- **Solution**: Add spikes before any processing steps
- **Reference**: Method 3500C, Sec 9.3.1 & Method 3550C, Sec 11.3

7 – Spike Additions (cont)

- **Method 3500C, Section 9.3.1**

"CAUTION: The utility of the data for the matrix spike compounds, as well as the surrogates and any other compounds spiked into any sample, depends on the degree to which the spiked compounds mimic the compounds already present in a field sample. Therefore, it is CRITICAL that any compounds added to a sample, including the surrogates, are added to the sample aliquot PRIOR TO any additional processing steps. This means that the matrix spike and surrogate compounds should be added to the sample PRIOR TO adding drying agents such as sodium sulfate to solid samples, or PRIOR TO making further adjustment to the pH of an aqueous sample, such as in a base/neutral extraction at pH >11."

7 – Spike Additions (cont)

- **Method 3550C, Section 11.3**

"NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing."

6 – MS/MSD

- **Problem**: Apply %R acceptance limits when [parent] > 1 ~ 4 x [spike]
- **Impact**: Bias
- **Rationale**: Misrepresentative bias
- **Solution**: Do not apply %R acceptance limits when [parent] > [spike]
- **Reference**: QSM Box D-12 & Method 8000C, Sec 9.5

6 – MS/MSD (cont)

- **QSM V3, Box D-12**

  "The concentration of the spiked compounds shall be at or below the midpoint of the calibration range or at the appropriate level of concern. If the native concentration is known, the MS/MSD should be <u>spiked 1 - 4 times</u> that concentration."

- ***QSM V4, (None)***

6 – MS/MSD (cont)

- **Method 8000C, Section 9.5**

"If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit or action level, the spike should be at or below the limit, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher. If historical data are not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries."

6 – MS/MSD (cont)

Example:

- [parent] = 100 ppb, [spike] = 40 ppb
- CLP NFG: [parent] < 4 x [spike] or limit not apply
- Uncertainty of [parent] = ± 30% or ± 30 ppb, which significantly affects [spike] = 40 ppb
- [spike] ≈ 1 ~ 5 x [parent] to minimize the impact of the uncertainty of [parent] on data bias (%R.) Data precision (RPD) is not impacted.

5 – LOQ/RL

- **Problem**: No precision and bias (P&B) specifications associated with LOQ/RL
- **Impact**: Precision & bias
- **Rationale**: Data without P&B cannot be used for reliable decision making
- **Solution**: P&B shall be determined and reported
- **Reference**: QSM Box C-8 (*Box D-14*)

5 – LOQ/RL (cont)

- **QSM V3, Box C-8**

  "The calculated mean and standard deviation must be at least as good as the DoD published limits, where they exist, or as good or better than the published limits for similar methods or technologies."

- ***QSM V4, Box D-14***

  "The laboratory procedure for establishing the LOQ must empirically demonstrate the precision and bias at the LOQ. The LOQ and associated precision and bias must meet client requirement and must be reported."

4 – LOQ

- **Problem**: Lowest calibration standard (LCalS) establishes LOQ w/o P&B
- **Impact**: Precision & bias
- **Rationale**: Most calibration standards not going through sample preparation and acceptance affected by calibration techniques
- **Solution**: Establish LOQ ≥ LCalS with documented P&B
- **Reference**: QSM App B & Box D-19 (*App B & Box D-14*)

4 – LOQ (cont)

- **QSM V3, Appendix B**

  "Limit of Quantitation (DoD Clarification): For DoD, the lowest standard of the calibration establishes the LOQ, but it must be greater than or equal to 3 times the LOD."

- ***QSM V4, Appendix B***

  "Limit of Quantitation (Clarification): The lowest concentration that produces a quantitative results within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard."

4 – LOQ (cont)

- **QSM V3, Box D-19**

  "For DoD, the quantitation range is defined by the low and high calibration standards and the low standard of the initial calibration curve (or the low-level calibration check standard for methods that require only one standard) establishes the LOQ. The LOQ must be at least three times the LOD. Results outside the quantitation range must be reported as estimated."

- ***QSM V4, Box D-14***

  "For DoD projects, the LOQ must be set within the calibration range prior to sample analysis. At a minimum, the LOQ must be verified quarterly. The laboratory procedure for establishing the LOQ must empirically demonstrate the precision and bias at the LOQ."

3 – CCV

- **Problem**: Questionable corrective actions for CCV failure
- **Impact**: Precision & bias
- **Rationale**: Different corrective action is needed for CCV failure due to random error, bad CCV standard, dirty injection port, calibration drift, etc.
- **Solution**: Take appropriate corrective actions and reanalyze associated samples.
- **Reference**: QSM Table B-1 (*Table F-1*), SW-846 Methods, & GLP

3 – CCV (cont)

- **QSM V3, Sec 5.5.10(e) – NELAC Standard**

"If the continuing calibration verification results obtained are outside established acceptance criteria, corrective actions must be performed. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then either the laboratory has to demonstrate acceptable performance after corrective action with two consecutive calibration verifications, or a new initial instrument calibration must be performed."

3 – CCV (cont)

Effect of Random Error on CCV with Normal Distribution, Control Limits = 80 – 120%, and σ = 5%

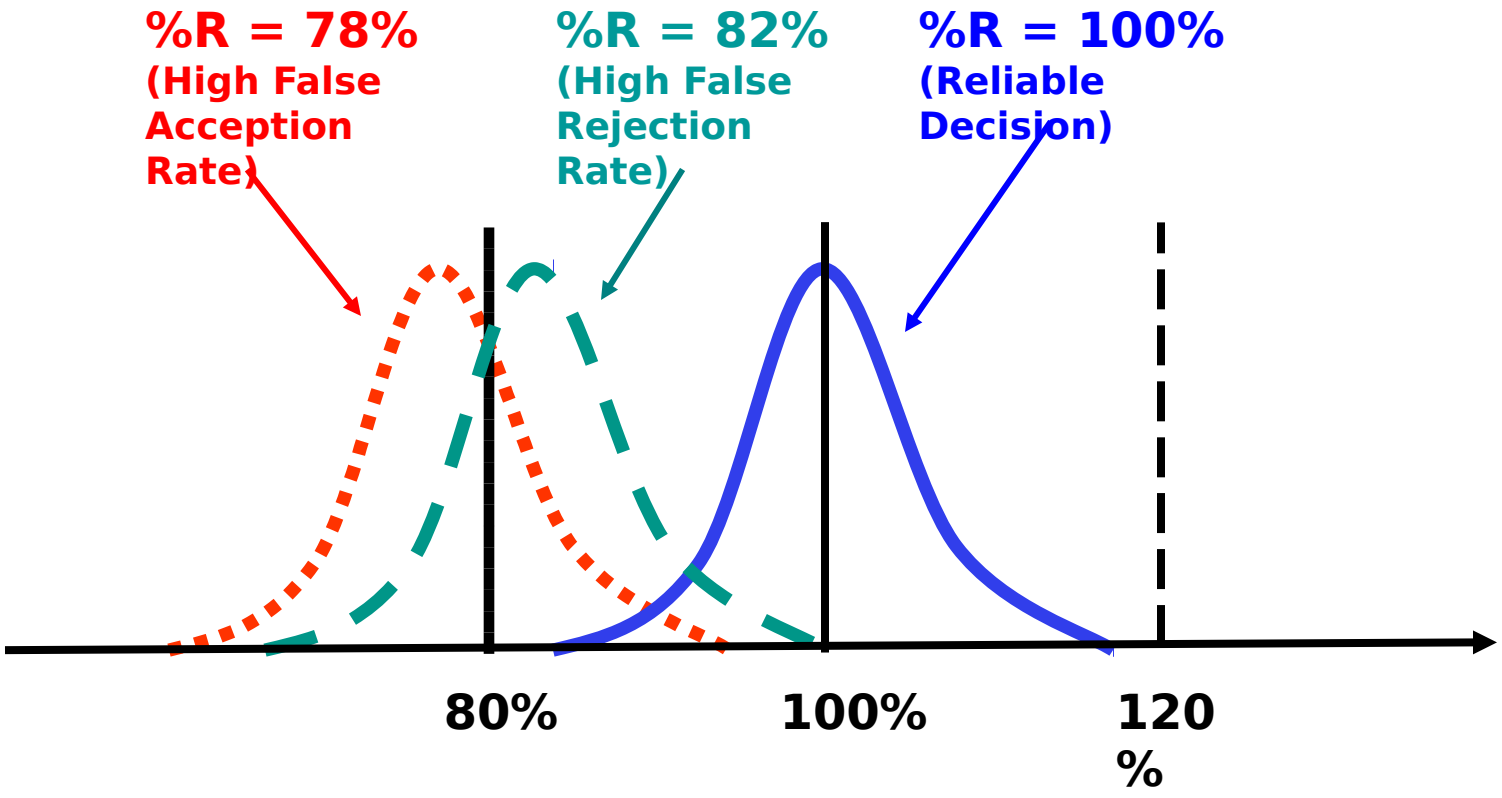
%R = 100%	%R = 78%	%R = 78%	%R = 82%
98.1	82.3	85.0	80.5
104.8	81.0	75.4	76.3
94.1	79.2	76.7	81.5
96.6	80.1	78.0	83.2
100.2	77.7	77.8	72.3
104.8	68.7	73.2	77.8
98.7	84.5	75.7	75.3
101.7	75.1	68.3	73.4
103.1	71.1	82.0	81.5
98.0	74.5	83.1	82.6
101.0	85.6	78.0	86.6
96.0	79.0	86.9	74.7
99.9	80.7	82.2	81.4
101.2	72.5	81.0	85.8
106.0	72.5	77.5	79.4

RED: False Acceptions

GREEN: True Acceptions

3 – CCV (cont)

Effect of Random Error on Decision of CCVs with Normal Distribution, Control Limits = 80 – 120%, and σ = 5%



3 – CCV (cont)

- **QSM V3, Table B-1 / *QSM V4, Table F-1***

  "If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging."

- ***QSM V4, Box 37***

  "The laboratory shall reanalyze CCVs and all samples analyzed since last successful calibration verification."

2 – Methanol Extract

- **Problem**: Methanol dilution effect is overlooked when using Method 5035
- **Impact**: Low biased results for samples with high moisture
- **Rationale**: Methanol extract is substantially diluted for samples with moisture > 10%
- **Solution**: Correct calculated concentration by solvent/water dilution factor
- **Reference**: Method 8000C, Sec 9.9 & 11.10.5

$$\mu L \text{ water } V_t = \frac{(mL \text{ of solvent}) + (\% \text{ moisture} \times g \text{ of sample})}{100} \times 1000 \, \mu L/mL$$

2 – Methanol Extract (cont)

- **Method 8000C, Section 9.9**

  "Solid samples with a significant moisture content (>10%) that are <u>extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture</u>. The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture determination."

- **Method 8000C, Section 11.10.5**

  Total Ext Volume = Solvent Volume + (% Moisture × Sample Weight)

1 – LCS

- **Problem**: Use client, contract, or method control limits for batch control when in-house limits fail
- **Impact**: Precision & bias
- **Rationale**: Lab performance and data quality are not reflected by control limits
- **Solution**: Improve in-house performance, use alternative methods or in-house control limits
- **Reference**: QSM App DoD-D, Sec D-7 (*App G, Sec G-7*)

1 – LCS (cont)

- **QSM V3, App DoD-D / QSM V4, App G**

  "Environmental testing laboratories that perform work for DoD must utilize the DoD-specified LCS control limits when assessing batch acceptance whenever they are available."

- **QSM V3, Section D-7 / QSM V4, Section G-7**

  "…it is important for laboratories to maintain their own in-house LCS limits. These in-house limits must be consistent with (i.e., within) the DoD limits (project-specific, if available; otherwise the following LCS-CLs). The laboratory in-house limits shall be calculated from the laboratory's historical LCS data in accordance with a documented procedure (e.g., SOP) that is consistent with good laboratory practice."

1 – LCS (cont)

- **QSM V3, Section D-7 / QSM V4, Section G-7**

  "Laboratories are expected to utilize their in-house limits as part of their quality control system, and to evaluate trends and monitor and improve performance."

  "When laboratories' in-house limits are outside the DoD control limits (upper and/or lower), they must report their in-house limits in the laboratory report (see Appendix DoD-A) even if the LCS associated with the batch in fact fell within the DoD limits. In this manner, DoD will be able to evaluate how laboratory performance affects the quality of the environmental data."

  "DoD may review the laboratory in-house limits and associated trends, as reflected in control charts, to determine whether the laboratory's overall performance is acceptable. If deemed unacceptable, this may be a basis on which DoD makes a decision to not use the laboratory again until substantial improvement has occurred."

Summary

- **Top 10 findings observed at > 90% of environmental labs assessed since 2005**
- **Good performance indicators for lab internal QA**
- **Maybe used for quick screening of contract labs**
- **Corrective actions must be taken prior to sample analysis**

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